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(54) **Gas generant compositions using dicyanamide salts as fuel.**

(57) A gas generant composition includes a fuel, at least 25 wt% of which is an alkali, alkaline earth, and/or transition metal salt of dicyanamide and an oxidizer which is an ammonium, alkali metal and/or alkaline earth metal salt of a chlorate, perchlorate or nitrate.

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nerant compositions suitab systems using dicyanamide salts ns, presently in use, use gas generant co of disadvantages with sodium azide, particularly insta , which presents a disposal problem for unfired gas generat generant systems and a number of non-azide formulations have 4,369,079 and 5,015,309, the teachings of which are incorporated , non-azide gas generants have not made significant commercial

sly proposed for non-azide gas-generants include salts of bitetrazole, lone, salts of nitrobarbituric acid, salts of nitroorotic acid, nitrouracil, amino-substituted guanidine, such as amino guanidine and triamino materials include not being commercially available or not being available ing hydrogen in their chemical structure. It is advantageous to have fuels o hydrogen in their chemical structure. Upon combustion, fuels that contain r. Water vapor could be disadvantageous to bag performance at cold tion. Heat capacity of the output gases is also increased with increased water s in burns to the vehicle occupant upon inflation of the bag.

979 to Jackson Jr. et al., the teachings of which are incorporated herein by e of cyanamide, dicyanodiamide (the dimerization product of cyanamide), and n gas generant compositions. While some of the salts of cyanamide and mercially available at a reasonable price and as salts of cyanamide contain no e disadvantage of not producing as great a quantity of gas upon combustion as her, they are not produced commercially in the purity that is required. The highest calcium cyanamide is 86 wt%, and the balance 14 wt% CaO renders the material Dicyanodiamide has the disadvantage of a high hydrogen content.

composition uses as at least a portion of the fuel component a compound which is an earth, or transition metal salt of dicyanamide or mixtures of alkali alkaline earth and/or alts. The gas generant composition further contains an internal oxidizer. omprises between about 10 and about 60 wt% of the gas generant composition. At least up to 100% of the fuel comprises a fuel selected from alkali, alkaline earth, and/or transition dicyanamide. From an availability standpoint, sodium dicyanamide is currently preferred. Calcium dicyanamide were more readily available, it would be preferred to sodium dicyanamide produces a readily filterable, non-reactive slag. Of transition metal dicyanamides, divalent metal dicyanamides are preferred, particularly cupric dicyanamide and zinc dicyanamide. The of the fuel may be an azide or non-azide fuel, added to adjust burn temperature and gas output. y, this other fuel is a non-azide fuel, such as those discussed above. Suitable cations may be potassium, sodium, magnesium, calcium, strontium, cerium and barium. In addition to these fuels ing no hydrogen, they are relatively non- toxic, and when formulated with an appropriate oxidizer, ce a non-toxic gas mixture upon ignition to inflate an automobile crash bag.

Transition metal dicyanamides have certain advantages over alkali/alkaline earth dicyanamide composi- ns.

For instance, cupric dicyanamide can be oxidized with an oxidizer such as a metal nitrate, e.g. trontium nitrate, to produce carbon dioxide, nitrogen and copper metal. When an alkali/alkaline earth dicyanamide, e.g. sodium dicyanamide, is combusted with an oxidizer such as strontium nitrate, the predicted products are carbon dioxide, nitrogen and a metal carbonate. The net result is higher gas yield from cupric dicyanamide, moles per 100 grams of generant. For instance, thermodynamic calculations performed by the Naval Weapons Center Propellant Evaluation Program (PEP) show that a stoichiometrically balanced mixture of strontium nitrate (68.1%) and sodium dicyanamide (31.9%) and strontium nitrate (36.6%) produce 1.61 moles of gas per 100 grams of generant. In addition to the higher gas yield, the resultant slag, copper metal, is easier to filter and more compatible than that produced by the doium dicyanamide fuel.

Similarly, zinc dicyanamide is better than sodium dicyanamide. Calculations show that a stoichiometrically balanced composition of zinc dicyanamide (34.14%) with strontium nitrate (65.85) produce 1.51 moles per 100 grams of generant which is higher than that produced by sodium dicyanamide and strontium nitrate.

The oxidizer, which is used at a level of between about 40 and about 90 wt% is selected from ammonium, alkalı metal and alkaline earth metal chlorates, perchlorates, nitrates and mixture thereof

Preferred oxidizers are nitrates.

Optionally, a portion of the oxidizer may be a transition metal oxide, such as iron oxide or cupric oxide. In addition to their oxidizing function, these oxides provide hard particles, facilitating compaction of the composition into pellets or other consolidated solid shapes. For pellitization purposes, it is preferred that between about 10 and about 50 wt% of the total oxidizer content be a transition metal oxide, particularly cupric oxide.

As is taught in U.S. Patent No. 5,139,588, the teachings of which are incorporated herein by reference, the cations of the fuel salts and oxidizers are preferably mixtures of alkali metal cations, i.e., lithium, sodium and potassium, and alkaline earth metal cations, i.e., magnesium, calcium, strontium, barium and cerium. Upon combustion, the alkali cations form liquid slag components and the alkaline earth metal cations form solid slag components, the mixture of liquid and solid salts forming clinkers which can be readily removed from the gas stream by filtration. The ratio of solid to liquid combustion slag components may be adjusted by the ratio of alkaline earth metal cations to alkali metal cations.

Alumina, silica or mixtures thereof may be added to scavenge corrosive alkali metal oxides, such as sodium oxide and potassium oxide. Accordingly, the composition of the present invention may contain alumina and/or silica at a level of between about 0.5 and about 30 wt%. The alumina and/or silica may be in the form of particulates or as fibers, such as fibers of various silica/alumina content. Alumina is generally preferred over silica, being a more efficient scavenger.

A binder is optionally added at a level of up to 10%, preferably at least about 0.5wt%. Suitable binder materials include but are not limited to molybdenum disulfide, graphite, polytetrafluroethylene, Viton ® (a copolymer of vinylidene fluoride and hexafluoropropylene), nitrocellulose, polysaccharides, polyvinylpyrrolidones, polycarbonates, sodium silicate, calcium stearate, magnesium stearate and mixtures thereof. Preferred binder materials are molybdenum disulfide and polycarbonates.

Alkali metal and alkaline earth metal carbonates and/or oxalates may optionally be added up to about 10 wt%. These act as coolants, lowering the combustion temperature. Lower combustion temperatures minimize production of toxic gases, such as CO and NO_x. Generally, if used, these coolants are used at a level of at least about 1 wt%.

As noted above, the alumina and/or silica may be in the form of fibers. Fibers help to mechanically reinforce the consolidated unburned material and subsequently consolidate slag material formed by burning the composition. Graphite fibers, e.g., up to about 10 wt%, typically at least about 1 wt%, may be also be used either alone as the sole fibrous material or in conjunction with other fibrous materials.

The invention will now be described in greater detail by way of specific examples.

Examples 1-4

Gas generant compositions in accordance with the invention are formulated as follows, all amounts being in weight %:

Example	1	2	3	4	
Component					Function
Sodium Dicyanamide	31.9	28.66	23	19	Fuel
Guanidine Nitrate			10	15	Co-Fuel
Strontium Nitrate	68.1	61.34	57	51	Oxidizer
Lithium Carbonate		5	10	15	Coolant
Aluminum Oxide		5			Slag Former
Thermochemical Calculations					
Tc* (°K)	2444	2039	1977	1831	
N_2 (mole/100g)	0.51	.77	.82	.81	
CO_2 (mole/100g)	0.49	.53	.47	.44	
H_2O (mole/100g)	0	0	.25	.34	

Example 5

A generant composition in accordance with the invention are formulated as follows, all amounts being in weight %:

Example	5	
Component		Function
Sodium Dicyanamide	20.69	Fuel
Guanidine Nitrate	11.76	Co-Fuel
Strontium Nitrate	48.00	Oxidizer
Lithium Carbonate	6.87	Coolant
Cupric Oxide	12.75	Co-oxidizer/binder
	100.00%	
Thermochemical Calculations		
Tc* (°K)	1947	
N_2 (mole/100g)	0.77	
CO_2 (mole/100g)	0.45	
H_2O (mole/100g)	0.29	

* Chamber Temperature

Examples 6 & 7

Examples of practical formulations of zinc and copper dicyanamide are shown in Table Ex. 6 and Ex.7 respectively. The compositions were prepared by mixing the materials in an aqueous slurry (approximately 25%), drying the composition, and screening the dried mixture. Burn rate slugs were pressed and burning rate measured at 1000 psi.

Table Ex. 6

Cupric Dicyanamide Formulations (Weight %)				
Mix	1	2	3	4
Component				
Cupric Dicyanamide	26.77	20.57	25.22	19.03
Guanidine nitrate	10	20	10	20
Lithium carbonate	10	10	10	10
Strontium nitrate	53.23	49.43	44.78	40.97
Cupric oxide	0	0	10	10
Thermochemical Calculations				
Rb (ips @ 1000 psi)	.75	.71	.67	.63
Moles/100 gm	1.70	1.95	1.60	1.86

Table Ex. 7

Zinc Dicyanamide Formulations (Weight %)		
Mix	1	2
Component		
Zinc dicyanamide	34.14	24.46
Strontium Nitrate	65.86	60.54
Lithium carbonate	0	5
Ammonium diliturate	0	10
Thermochemical Calculations		
Rb (ips @ 1000 psi)	0.65	0.7
Miles/100 gm.	1.51	1.60

Claims

1. A gas generant composition comprising between 10 and 60 wt% of a fuel, at least 25 wt% up to 100% of which is selected from alkali, alkaline earth, and transition metal salts of dicyanamide and mixtures thereof, balance other fuel and

   between 40 and 90 wt% of an oxidizer selected from ammonium, alkali metal and alkaline earth metal chlorates, perchlorates, nitrates and mixtures thereof.

2. A gas generant composition according to claim 1, further containing between 0.5 and 10 wt% of a binder.

3. A gas generant composition according to claim 2 wherein said binder is selected from molybdenum disulfide, graphite, polytetrafluoroethylene, vinyl fluoride/hexafluoropropylene copolymer, nitrocellulose, polysaccharides, polyvinylpyrrolidones, polycarbonates, sodium silicate, calcium stearate, magnesium stearate and mixtures thereof.

4. A gas generant composition according to claim 2 wherein said binder comprises molybdenum disulfide or a polycarbonate.

5. A gas generant composition according to any preceding claim further containing between 1 and 10 wt% of a coolant selected from alkali metal and alkaline earth metal carbonates, oxalates and mixtures thereof.

6. A gas generant composition according to any preceding claim further containing between 1 and 10 wt% of graphite fibers.

7. A gas generant composition according to any preceding claim further containing between 0.5 and 30 wt% alumina and/or silica.

8. A gas generant composition according to any preceding claim containing, in addition to said salt(s) of dicyanamide, up to about 50 wt% of a fuel selected from salts of bitetrazole, aminotetrazole, nitrotriazolone, triazolone, salts of nitrobarbituric acid, salts of nitroorotic acid, nitrouracil, salts of guanidine, salts of amino-substituted guanidine, and mixtures thereof.

9. As gas generant composition according to any preceding claim wherein said salt of dicyanamide is sodium dicyanamide.

10. A gas generant composition according to any one of claims 1 to 8 wherein said salt of dicyanamide is calcium dicyanamide.

11. A gas generant composition according to any one of claims 1 to 8 wherein said salt of dicyanamide is cupric dicyanamide.

12. A gas generant composition according to any one of claims 1 to 8 wherein said salt of dicyanamide is zinc dicyanamide.

13. A gas generant composition according to any preceding claim wherein between 10 and 50 wt% of said oxidizer comprises a transition metal oxide or a mixture of transition metal oxides.

14. A gas generant composition according to Claim 13 wherein said transition metal oxide is ferric oxide, cupric oxide or a mixture thereof.

15. A gas generant composition according to claim 14 wherein said transition metal oxide is cupric oxide and said dicyanamide salt is cupric dicyanamide.

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EUROPEAN SEARCH REPORT

Application Number
EP 94 30 8331

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
D,A	US-A-4 386 979 (C.H. JACKSON, JR.) * column 2, line 30 - column 3, line 57 *	1	C06D5/06 C06B43/00
A	EP-A-0 519 485 (DYNAMIT NOBEL AKTIENGESELLSCHAFT) * claims *	1	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)
C06D C06B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	30 June 1995	Schut, R

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
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E : earlier patent document, but published on, or after the filing date
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